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**Ion Modulated Electroactivity in Thin-film Polymers Derived from
Bipyridyl and Phenanthroline Complexes of Iron**

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13. ABSTRACT (Maximum 200 words) Profound changes in the metal-centered electroactivity of thin-film redox polymer/electrolyte systems accompany the replacement of a conventional electrolyte solution (aqueous tetraethylammonium perchlorate) by any of several aq. $\text{CH}_3(\text{CH}_2)_n\text{SO}_3\text{Na}^+$ solutions. For example for a poly- $\text{Fe}(4\text{-methyl-4'-vinyl-2,2'-bipyridine})_3^{3+}$ film in contact with an aq. sodium decanesulfonate solution: a) the overall redox capacity decreases by roughly half an order of magnitude, b) the rate of hopping-based electron transport during charging decreases by 20-fold, and c) the thermodynamic potential for metallopolymer oxidation moves to a significantly less positive value, in comparison to films equilibrated with conventional solutions. Further experiments show that the modulation behavior is associated with the uptake and release of charge-compensating anions during film oxidation and reduction (i.e. cations are excluded), that the degree of modulation increases with increasing counter anion size, and that the modulation phenomenon is chemically reversible. These unusual effects are tentatively attributed to polymer-based steric constraints on large alkanesulfonate ion incorporation, together with hydrophobic partitioning effects. These factors apparently conspire to couple film-based electron motion strongly to counter-anion motion. Finally, spectroelectrochemical measurements show that $\text{CH}_3(\text{CH}_2)_n\text{SO}_3^-$ -containing films are reversibly confined to a predominantly mixed-valent form ($\text{Fe(II)} + \text{Fe(III)}$), even at electrochemical potentials far removed from the formal potential for redox processes in the film.					
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Introduction

Uses (or potential uses) of polymeric redox conductors¹ in such areas as electrochromics,² diagnostic and analytical sensing,³ and electrocatalysis⁴ suggest a need for a detailed understanding of mechanisms of conductivity. While it is generally acknowledged that electrons diffuse through redox polymers via a series of hopping events,⁵ the exact role of charge compensating counter ions is unclear. Available theory implies that intrapolymer ionic and electronic motion should be strongly correlated⁶ yet there are only a handful of experimental observations to support this contention.⁷ In the current study, some unusual and apparently unprecedented electrochemical effects, indicative of strong electron-ion coupling, have been uncovered. These effects are described below, together with preliminary explanations.

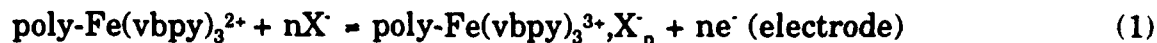
Experimental

Polymer films were prepared on glassy carbon surfaces via electropolymerization of either $[\text{Fe}^{\text{II}}(\text{vbpy})_3](\text{PF}_6)_2$ (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine)⁸ or $[\text{Fe}(\text{NH}_2\text{-phen})_3](\text{NH}_2\text{-phen} = 5\text{-amino-1,10-phenanthroline})$.⁹ Continuous cycling between -0.5 V and -2.0 V, or +0.3 V and +1.9 V (vs. s.s.c.e.), in acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate (TEAP) and approximately 2 mM monomer, produced adherent red films.¹⁰ To achieve electrolyte solubility, subsequent measurements were made in water as solvent. These measurements, as well as the initial electrochemical syntheses, were performed with a PAR 273 potentiostat by using a standard three electrode arrangement (glassy carbon working electrode (0.07 or 0.008 cm² disk),

platinum wire counter electrode and saturated (NaCl) calomel reference electrode). Spectroelectrochemical measurements were made with an HP Model 8452A diode array spectrophotometer by using indium-tin oxide coated glass (Delta Technologies) as the working electrode. All alkanesulfonates were purchased from Aldrich and used as received. TEAP (GFS Chemicals) was recrystallized from purified distilled water (Millipore system) and dried *in vacuo*. Acetonitrile (Fisher) was distilled in glass and stored over molecular sieves.

Results and Discussion

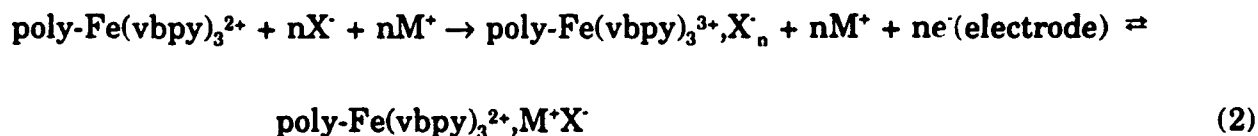
Metal centered oxidation and reduction of thin-film polymers necessarily involves the uptake and release of charge-compensating ions from the external electrolyte solution, e.g.:



We have observed that replacement of TEAP by 1-decanesulfonic acid, sodium salt (DSA) as the electrolyte has enormous effects upon thin film (i.e., poly-Fe(vbpy)₃^{m+} and poly-Fe(NH₂-phen)₃^{m+}) electroactivity. As shown by Figure 1, electrolyte replacement leads to a reversible – roughly factor of four – decrease in film redox capacity or electrochemical accessibility. Related mixed electrolyte studies show that the full modulation effect can be induced by as little as 5 mM of the decanesulfonate in a 95 mM TEAP solution. We interpret the results as strong evidence for preferential partitioning of the DSA anion into the polycationic film framework – where presumably the preference reflects differential hydrophobic interactions.

The magnitude of the electroactivity attenuation effect is significantly dependent upon film thickness. For example, a polymer film that is grown exhaustively from a 2 mM solution (>50 electrochemical scans; limiting coverage of ca. 500 monolayer equivalents) exhibits a much greater change in current response than a film grown for only 10 scans (coverage of ca. 100 monolayer equivalents). On the other hand, thinner films exhibit fewer memory and time effects than the thicker (and presumably more cross-linked) assemblies. The extent of modulation also depends upon the alkyl chain length. A series of voltammetry studies with poly-Fe(vbpy)₃^{m+} and CH₃(CH₂)_nSO₃⁻Na⁺ electrolytes (n = 0-11; see Figure 2) shows a systematic decrease in electroactivity with increasing chain length (where relative magnitude of the electroactivity decrease is essentially unaffected by factor of 10 changes in voltammetry sweep rate).

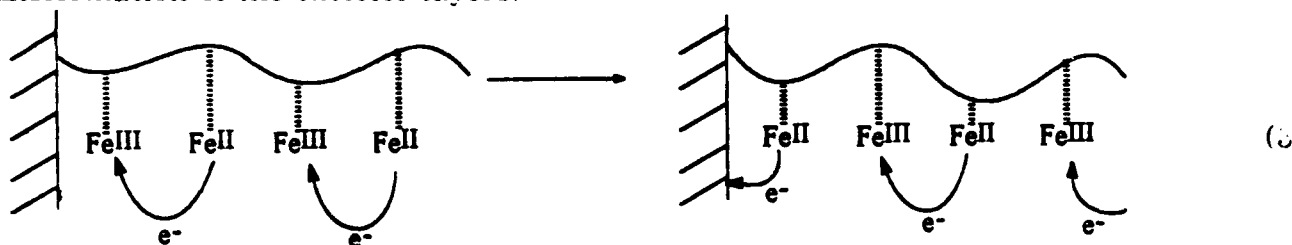
These experiments, as well as the mixed electrolyte measurements, are obviously suggestive of a film reaction that involves anion uptake during metal oxidation (eq. 1), with uptake driven, in part, by hydrophobic interactions. The unusual film-based redox effects are then reasonably ascribed to steric phenomena. Conceivably, however, if the initial hydrophobic partitioning of CH₃(CH₂)_nSO₃⁻ were sufficiently strong, subsequent ion release (during film reduction) would not occur. Electroneutrality would instead be achieved by electrolyte *cation* incorporation:



To evaluate this possibility, we measured film redox potentials as a function of electrolyte concentration in each of several electrolytes (including TEAP and DSA). After

correction for small liquid junction potentials associated with the s.s.c.e. reference,¹¹ we found that the poly-Fe(vbpy)₃^{3+/2+} potential shifted in the negative direction by 58 to 68 mV per decade increase of electrolyte concentration (independent of electrolyte identity).¹² If the metallopolymer behaved as a perfect cation-exclusion membrane (i.e. anion uptake only), rigorous Donnan behavior (-59.2 mV per decade) would have been seen.¹³ Our results clearly are sufficiently close to the ideal that only anions can be participating significantly in the film charging and conduction processes.

With the identity of the charge compensating ion now more satisfactorily established, it is appropriate to consider the dynamics of eq. 1. For all but the first "monolayer" of the metallopolymeric film, oxidation and reduction must occur by a site-to-site hopping process, such that the interior of the film mediates the electrochemical transformation of the exterior layers:



With fixed redox sites, the hopping-based film oxidation (or reduction) process can be viewed as an electron diffusion process. The hopping dynamics can then be described phenomenologically by a charge transfer diffusion coefficient, D_{ct} .^{1a,5,14} Transient measurements (chronoamperometry) of electron diffusion reveal a substantial electrolyte anion dependence. For example, in aqueous .05M TEAP solutions D_{ct} is $\sim 3 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$, but only $\sim 1.5 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ in .05M aq. DSA.¹⁵ (It should be noted that dynamic electrolyte effects of this magnitude generally are *not* seen when the identity of the

charge compensating ion is varied.¹⁶⁾ Further studies with other $\text{CH}_3(\text{CH}_2)_n\text{SO}_3^-$ species show that D_{et} systematically decreases as the alkyl chain length increases (with the most pronounced effects found for $n > 4$). While a detailed mechanistic explanation is lacking, it seems reasonable to ascribe the diminution of apparent electron transport rates with increasing anion size to polymer-based steric constraints on coupled anion motion. In any case, counter anions clearly are modulating the overall kinetics of electron transport within the thin-film environment.

Figure 3 shows that the ion modulation effects extend to the polymer-film redox thermodynamics. The apparent formal potential (E_f) for (metal-based) polymer oxidation (determined from cyclic voltammetry peak potentials at limiting low sweep rates) exhibits a systematic negative shift with increasing n , for $n = 5$ to 11 – but essentially no dependence for $n = 0$ to 4. The shifts imply an increasing preference for alkanesulfonate incorporation in film (Fe) oxidation state III versus II, with increasing alkane size. (There is, of course, a compelling electrostatic basis for enhanced partitioning of counter anions into $\text{poly-Fe}^{\text{III}}(\text{vbpy})_3^{3+}$ versus $\text{poly-Fe}^{\text{II}}(\text{vbpy})_3^{2+}$; the formal potential shifts simply indicate that the extent of the enhancement increases as n increases.) While these types of effects appear to be largely unprecedented for fixed-cation frameworks, they have been encountered previously with a fixed-anion system (specifically, the nickel/ferrocyanide polymer developed by Bocarsly and co-workers(7b, c)). In the anionic system, E_f was found to be tremendously sensitive to the size of the charge-compensating cation (typically an alkali metal ion). The sensitivity was attributed, in part, to the potentially extreme lattice structural demands associated with cation incorporation in the

semicrystalline film assembly.(7b, c) In view of the greater linkage lengths, enhanced linkage flexibility and apparently greatly decreased crystallinity of poly-Fe(vbpy)₃^{m+} films, a similar explanation is probably not applicable here. As an (admittedly speculative) alternative, we propose that uptake of longer chain alkanesulfonates by poly-Fe(vbpy)₃²⁺ creates an increasingly lipophilic film environment (perhaps, in part, by physical displacement of water molecules). The increased lipophilicity then offers a progressively more inviting environment for an additional (hydrophobic) anion when the framework is oxidized. Presumably, systematic studies of solvent swelling would offer at least qualitative indication of the validity of the explanation.

Finally, spectroelectrochemical experiments provide compelling evidence that the observed ion-induced losses of film electroactivity are related to reversible trapping of the polymer in a mixed valence form. Spectral interrogation of polymer metal-center oxidation-state distribution is possible when film growth is carried out with a conductive glass electrode. Particularly instructive are optical measurements at 520nm, where Fe^{II}L₃²⁺ (but not Fe^{III}L₃³⁺) absorbs strongly. As expected, the absorbance at 520nm (in TEAP as electrolyte) is maximized (see Figure 4a) when the film is held at potentials significantly negative of the formal potential (i.e. at strongly reducing potentials), but is minimized – and indeed, completely bleached – when the film is subjected to oxidizing potentials. In striking contrast, the bleaching process as well as subsequent recovery, is substantially inhibited (Figure 4b) for a film equilibrated in a DSA-containing solution (2.5 mM DSA + 47.5 mM TEAP). (Equilibration, as indicated by an unchanging spectral response, was achieved after four oxidation/reduction cycles.) Thus, the metallopolymer

becomes trapped in a largely mixed-valent form – with changes in the external electrochemical potential causing only modest excursions away from mixed-valency. (It is worth noting that mixed valency persists even when the film is held at net oxidizing (or reducing) potentials for 30 minutes or more.) Nevertheless, the full spectroelectrochemical response (Fig. 4a) can be restored (or nearly restored) by re-equilibrating the film with a DSA-free solution.

The observation of nearly complete mixed-valence confinement in DSA-containing solutions is consistent with the almost complete loss of cyclic voltammetric response in the same solutions (Fig. 1). Furthermore, the observation indicates that the voltammetry effect is not merely the result of a short timescale kinetic phenomenon. Indeed, the persistence of the mixed-valence state suggests that it may be related in a fundamental way to the overall steric limitations presumably imposed by the cationic polymer film on the anion uptake process.¹⁷ Perhaps more intriguing are the implications of mixed valency for steady-state film conductivity. The presence of both donor (Fe (II)) and acceptor (Fe(III)) sites at potentials far removed from E_f suggests that DSA-containing films may be conductive over a very wide potential window and that it may be possible to drive conduction by electric field gradients (as in many organic conducting polymers), rather than by chemical potential gradients (i.e. donor and acceptor concentration gradients) as in conventional redox polymers.^{1a,5,18} Experiments designed to evaluate these unusual possibilities are currently underway.

Conclusions

The substantial changes in polymer film electroactivity (i.e. redox capacity, charging kinetics, and electrochemical thermodynamics) induced by counter-ion size manipulation are unusual and, apparently, largely unprecedented. The microscopic origin of the changes may lie in ion-gated electron hopping effects, hydrophobic/hydrophilic effects, ion trapping effects or, perhaps more likely, some combination of the above. Further studies, including steady state conductivity assessment, electrochemical quartz crystal microbalance measurements and Auger spectroscopy studies, are planned, and should eventually resolve the remaining mechanistic questions.

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 10. Electrochemical reduction of $\text{Fe}(\text{vbpy})_3^{2+}$ leads to polymerization based on vinyl

radical generation and propylene linkage formation. (8b) The chemical basis for polymer formation following $\text{Fe}(\text{NH}_2\text{-phen})_3^{2+}$ electrooxidation is amine radical cation generation, followed by proton loss and diazo linkage formation.(9)

11. The magnitude of the correction was -13 mV per decade of electrolyte concentration (J. Redepenning, Personal communication).
12. Control experiments with monomeric $\text{Fe}(\text{vbpy})_3^{3+/2+}$ in solution revealed almost no dependence of E_r on electrolyte concentration and only a marginal dependence on electrolyte identity (i.e., slight shifts toward more *positive* values with increasing alkanesulfonate anion size).
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15. D_a diminution is also observed in mixed electrolytes (TEAP + DSA).
16. An exception is the nickel-containing prussian blue system developed by Bocarsly and co-workers.^{7b, c}
17. This explanation is perhaps sufficient to account for incomplete Fe(III) formation at potentials positive of E_r . At potentials *negative* of E_r , however, mixed-valence confinement (rather than exclusive Fe(II) formation) implies the existence of a very large driving force (hydrophobic phenomena?) for "excess" alkanesulfonate

retention.

18. Electric field driven conductivity has been observed previously with redox polymers at very low temperatures (in the absence of solvent)^{7a} and under unusual circumstances where counter cations were physically excluded from a formally mixed-valent assembly (Elliott, C. M.; Redepenning, J. G.; Balk, E. M. *J. Am. Chem. Soc.* **1985**, *107*, 8302).

Figure Captions

1. Poly-Fe(vbpy)₃^{3+/2+} film voltammetry (100 mV/sec): (a) in 0.05 M TEAP (solid line), followed by 0.05 M DSA (dashed line), and (b) in 0.05 M DSA, followed by 0.05 M TEAP. Electrode area: 0.008 cm².
2. Charge passed during poly-Fe(vbpy)₃³⁺ film electroreduction as a function of electrolyte composition: filled circle = 0.05 M TEAP; open circles = 0.05 M CH₃(CH₂)_nSO₃Na⁺. Electrode area: 0.07 cm². Sweep rate = 100 mV/sec.
3. Dependence of E_r for poly-Fe(vbpy)₃^{3+/2+} films on electrolyte composition: filled circle = 0.05 M TEAP; open circles = 0.05 M CH₃(CH₂)_nSO₃Na⁺ (except 0.01 M for n = 11, due to solubility limitations). Electrode area: 0.07 cm². Sweep rate = 100 mV/sec. Limiting slow sweep rates (1 mV/sec) produce nearly identical results.
4. Spectroelectrochemical response of a poly-Fe(NH₂-phen)₃^{3+/2+} film at 0 V (solid line) and 1.5 V (dashed line) in: (a) 0.05 M TEAP, and (b) 0.05 M TEAP + 0.0025 M DSA electrolyte solutions.

